

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Mihoko Ohashi et al

Group Art Unit: 1796

Serial Number: 10/524,259

Examiner: BERMAN, SUSAN W

Filed: February 11, 2005

For: OPTICAL MATERIAL CONTAINING PHOTO-CURABLE
FLUORINE-CONTAINING POLYMER AND PHOTO-CURABLE
FLUORINE-CONTAINING RESIN COMPOSITION

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner

Washington, D.C. 20231

Sir,

Takayuki ARAKI, citizen of Japan, duly deposes and says:

1. That he has graduated from the master course of Kyoto Institute of Technology, Japan, in the year of 1986;

2. That he was employed in his capacity since 1986 by DAIKIN INDUSTRIES, LTD.;

3. That he has been engaged in research and development on preparation of functional fluorine-containing polymer;

4. That he has read and is familiar with the instant application for United States Letters Patent and the Office Action thereto mailed October 9, 2007;

5. That he experimented and proved that according to the photo-curable fluorine-containing resin composition comprising the

photo-curable fluorine-containing polymer of the present invention (USSN 10/524,259), when irradiating UV ray after forming a film, the obtained coating film has higher strength and remarkably improved surface hardness than a coating film prepared from a resin composition according to US 6,790,587.

EXPERIMENTAL

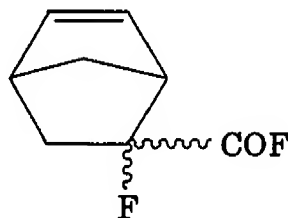
A polymer in US'587 and a fluorine-containing polymer used in the present invention were synthesized respectively, and were mixed with a photoacid generator to prepare resin compositions.

Then using each one of the compositions, the coating films were prepared and their physical properties after UV irradiation were compared.

EXPERIMENT 1 [Synthesis of fluorine-containing polymer in the cited reference of US'587]

(Synthesis of (2-fluoro-5-norbornene-2-yl)-1,1,1,3,3,3-hexafluoro-2-propanol (NB-2))

A 100 ml three-necked flask equipped with a thermometer, cooling tube having a 3-way cock and dropping funnel was charged with 27.7 g (168 mmol) of 2-fluoro-5-norbornene-2-carboxylic fluoride (NB-1):

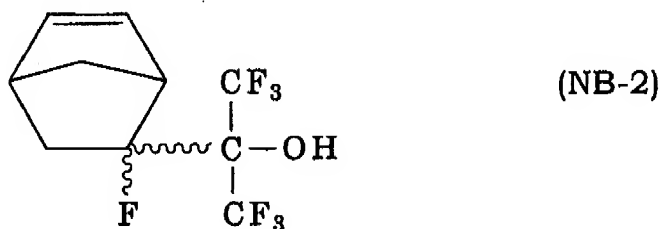


(NB-1)

and 28 g (482 mmol) of potassium fluoride and was cooled in ice bath

in nitrogen gas atmosphere.

While maintaining the inside temperature of the flask at a temperature of from 3° to 10°C, 62 g (436 mmol) of CF_3SiMe_3 was added dropwise to this solution over two hours with stirring, and after the reaction temperature was raised to room temperature, stirring was continued overnight. Then the resulting reaction solution was poured into ice water, followed by extracting with diethyl ether. After washing the organic phase with water, diluted hydrochloric acid, and then, saturated sodium bicarbonate solution, the organic phase was dried with calcium chloride. Then refining was carried out by distillation under reduced pressure and 50 g (yield: 80 %) of (2-fluoro-5-norbornene-2-yl)-1,1,1,3,3,3-hexafluoro-2-propanol (NB1):



was obtained.

Physical properties of the product were as follows.

^{19}F -NMR (solvent: CDCl_3):

endo-form: -156.7 (m, F), -72.3 (m, CF_3), -72.0 (m, CF_3)

exo-form: -152.2 (m, F), -73.8 (m, CF_3), -72.5 (m, CF_3)

^1H -NMR (solvent: CDCl_3): 6.60-6.23 (1H, m, sp^2CH), 6.10-5.86 (1H, m, sp^2CH), 4.34-3.80 (1H, s broad, OH), 3.80-3.47 (m, 1H), 3.37-2.98 (1H, s), 2.98-2.54 (1H, s), 2.5-2.15 (1H, t), 2.10-1.61 (2H, m)

MS: 241 ($\text{M}^+ - \text{FH}_2\text{O}$), 221, 201, 66 (C_5H_6)

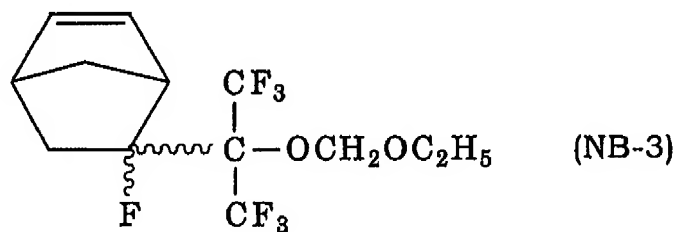
IR: 3500 cm^{-1} (O-H), 1590 cm^{-1} (C=C)

(Introduction of protecting group)

A 100 ml four-necked flask equipped with a reflux condenser, thermometer, stirrer and dropping funnel was charged with 3.5 g of sodium hydride (purity: 60 %) and 10 ml of tetrahydrofuran, and while maintaining the inside temperature of the flask at a temperature of from 5° to 10°C, 2.1 g of norbornene derivative (NB-2) having $-\text{C}(\text{CF}_3)_2\text{OH}$ group obtained above was added dropwise over one hour. After completion of the addition, stirring was carried out at room temperature for 1.5 hours. Then thereto was added dropwise 9.6 g of chloromethyl ethyl ether ($\text{ClCH}_2\text{OC}_2\text{H}_5$) over one hour. After completion of the addition, stirring was carried out at room temperature for five hours.

After terminating the reaction, water was added thereto, an organic substance was extracted with ether, and the ether layer was washed with saturated NaHCO_3 aqueous solution, followed by drying with anhydrous magnesium sulfate.

After drying, ether was distilled off, and 20.5 g (yield: 77 %) of norbornene derivative (NB-3):



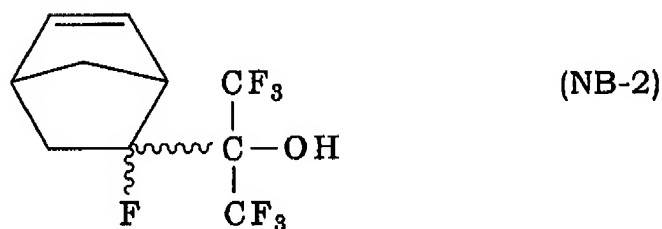
(melting point: 58° to 60°C/1.5 mmHg) having $-\text{OCH}_2\text{OC}_2\text{H}_5$ group was obtained by distillation under reduced pressure.

The above-mentioned structure of this compound was identified

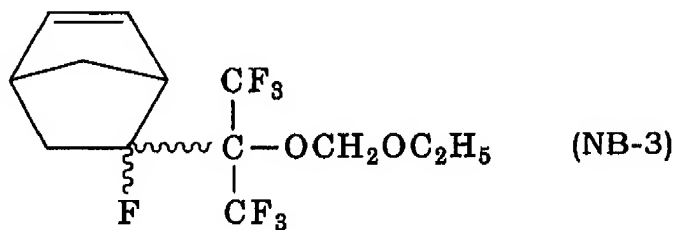
by GC-Mass, ^{19}F -NMR and ^1H -NMR analyses.

(Synthesis of copolymer of tetrafluoroethylene (TFE), the fluorine-containing norbornene derivative (NB-2) having $-\text{OH}$ group, and the fluorine-containing norbornene derivative (NB-3) having $-\text{OCH}_2\text{OC}_2\text{H}_5$ group)

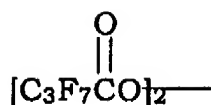
A 500 ml autoclave equipped with a valve, pressure gauge, stirrer and thermometer was charged with 19.5 g of fluorine-containing norbornene derivative (NB-2):



having $-\text{OH}$ group, 10.1 g of fluorine-containing norbornene derivative (NB-3):



having $-\text{OCH}_2\text{OC}_2\text{H}_5$ group, 250 ml of HCFC-141b and 6.5 g of perfluorohexane solution of 8.0 % by weight of heptafluorobutanoyl peroxide:



, and the inside of a system was sufficiently replaced with nitrogen gas. Then 52.5 g of TFE was introduced through the valve, followed by reacting at 40°C for 12 hours. With the advance of the reaction, the gauge pressure was lowered from 0.96 MPaG (9.7 kgf/cm²G) to 0.91 MPaG (9.2 kgf/cm²G).

After discharging the un-reacted monomer, the polymerization reaction solution was taken out, and, after concentrating, re-precipitation was carried out with hexane to separate a copolymer. Vacuum drying was carried out until a constant weight to obtain a copolymer (7.2 g).

As a result of ¹H-NMR and ¹⁹F-NMR analyses, the copolymer was identified as a copolymer of TFE/fluorine-containing norbornene derivative (NB-2) having -OH group/fluorine-containing norbornene derivative (NB-3) having -OCH₂OC₂H₅ group (= 50/35/15 % by mole).

According to GPC analysis, a number average molecular weight thereof was 4,000.

EXPERIMENT 2

[Synthesis of fluorine-containing polymer according to the present invention]

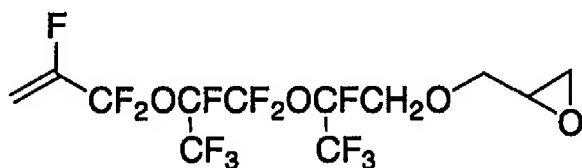
(Synthesis of fluorine-containing allyl ether having glycidyl group)

Into a 500 ml four-necked glass flask equipped with a stirrer and thermometer were poured 200 g of perfluoro-(1,1,9,9-tetrahydro-2,5-bistrifluoromethyl-3,6-dioxanonenol), 2 ml of water and 114 g of epichlorohydrin, followed by heating to 60°C.

To this solution was added NaOH in ten lots with a pellet. Then the reaction solution was heated to 80°C and reaction was carried out for six hours.

After completion of the reaction, hydrochloric acid was poured into the solution for neutralization and then the solution was poured into a separating funnel, followed by washing with water and saturated brine, drying with anhydrous magnesium sulfate and separating the solution by filtering. The solvent was distilled off from the filtrate by an evaporator. As a result of distillation of the reaction solution, 139 g of distillate was obtained. A boiling point thereof was 48° to 55°C (0.04 mmHg).

According to ¹H-NMR, ¹⁹F-NMR and IR analyses, the obtained product was identified as a fluorine-containing allyl ether of the structure:



having glycidyl group.

¹H-NMR analysis data (in δ(ppm) CDCl₃):

5.15 - 4.90 (2H, m), 4.05 - 3.85 (2H, m), 3.85 - 3.75 (1H, m), 3.38 - 3.25 (1H, m), 2.98 - 2.92 (1H, m), 2.68 - 2.57 (1H, m), 2.45 - 2.38 (1H, m)

¹⁹F-NMR analysis data (in δ(ppm) CDCl₃, R-11 internal standard):

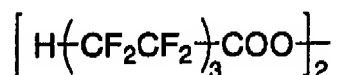
-72.6 - -73.0 (2F, m), -79.4 - -81.6 (8F, m), -124.0 - -124.4 (1F, m), -132.8 - -133.2 (1F, m), -145.1 - -145.6 (1F, m)

IR analysis data (cm⁻¹)

1695 ($\nu_{C=C}$)

(Synthesis of fluorine-containing allyl ether polymer having glycidyl group)

Into a 50 ml four-necked glass flask equipped with a stirrer and thermometer were poured a solution of 10.0 g of fluorine-containing allyl ether having glycidyl group synthesized in Preparation Example 3 and 8 g of HFC-365 ($CF_3CH_2CF_2CH_3$), and then 3.8 g of perfluorohexane solution of 8.0 % by weight of:



and after sufficiently replacing the inside of the flask with nitrogen gas, stirring was continued at 20°C in a stream of nitrogen gas for nine hours and a solution having a high viscosity was obtained.

To the obtained solution was poured a sodium bicarbonate solution for neutralization, followed by dissolving in diethyl ether. The resultant solution was poured into a separating funnel, followed by washing with water and saturated brine. The organic layer was dried with anhydrous magnesium sulfate, and magnesium sulfate was separated by filtering. The solution was concentrated and poured into hexane solution for re-precipitation, and the solution was separated to obtain a colorless transparent polymer. This polymer was again dissolved in diethyl ether to make 22.6 % by weight of solution (19.7 g).

According to 1H -NMR, ^{19}F -NMR and IR analyses, the polymer was identified as a fluorine-containing polymer which consisted of the

structural unit of the above-mentioned fluorine-containing allyl ether having glycidyl group and had the glycidyl group at an end of its side chain. Also according to GPC analysis using tetrahydrofuran (THF) as a solvent, a number average molecular weight of the polymer was 13,000, and a weight average molecular weight thereof was 35,000.

EXPERIMENT 3

[Preparation of photoresist (US'587), photo-curable fluorine-containing resin composition (present invention), and coating films]

(1) Production of photoresist (US'587)

To 5.12 g of methyl amyl ketone were added 0.3 g of methyl amyl ketone solution of 5 % by weight of triphenylsulfonium trifluoromethylsulfonate (=triphenylsulfonium triflate) as a photoactive compound and 0.46 g of the fluorine-containing polymer synthesized in EXPERIMENT 1, and stirred to obtain uniform solution 1 (photoresist).

(2) Production of photo-curable resin composition (present invention)

To the fluorine-containing polymer prepared in EXPERIMENT 2 (in diethyl ether solution at the polymer concentration of 22.6 % by weight) was added methyl isobutyl ketone (MIBK) for diluting and adjusting the polymer concentration to 5.0 % by weight.

To 10 g of the obtained polymer solution was added 2.5 g of a solution obtained by dissolving, in MIBK, MPI-103 (trade name, 4-methoxyphenylphenyl iodonium hexafluoro antimonate available from Midori Kagaku Kabushiki Kaisha) as a photoacid generator at a concentration of 1 % by weight, and stirred to obtain uniform solution

2 (photo-curable resin composition).

(3) Preparation of coating films 1 and 2 and UV irradiation

After the solutions 1 and 2 were filtered by 0.45 μm PTFE membrane, acryl panels (black) having an un-treated surface were spin-coated with the solutions 1 and 2 at room temperature, and then vacuum-dried at 100°C for one minute to give coating films 1 and 2, respectively. In that case, a rotation speed of a spin coater was adjusted between 1,000 and 2,000 rpm so as to be a thickness of dried coating film within a range of from 90 to 110 nm.

No unevenness was observed on the surface of the coating films 1 and 2, and both coating films 1 and 2 showed uniform and favorable external appearance.

Then the dried coating films 1 and 2 were irradiated with ultraviolet light at an intensity of 1,500 mJ/cm² in the air at room temperature by using a high pressure mercury lamp.

EVALUATION AND RESULTS

[Evaluation of physical properties of coating film]

The following physical properties of the coating films 1 and 2 obtained in (3) of EXPERIMENT 3 were evaluated before and after UV irradiation.

(1) Reflectance of one side of film

After UV irradiation, the acryl plate provided with the coating film was set on a visible ultraviolet light spectrophotometer equipped with a 5° regular reflection unit, and a reflectance was measured with

light having a wavelength of 589 nm. The results are shown in Table 1.

(2) Pencil hardness

Measured according to JIS K5400.

(3) Solvent resistance

After the surface of the coating film was rubbed with a cotton cloth impregnated with ethyl acetate, condition (dissolved or peeled) of the coating film surface was evaluated with naked eyes.

The evaluation was made by:

○: No change

△: Partly dissolution or peeling

×: Dissolution or peeling

(4) Alkali resistance

The film was immersed in a 2N aqueous solution of KOH of 60°C for one minute and the condition of the film was observed with naked eyes and hardness was measured according to pencil hardness of (2) above.

The evaluation was made by:

○: No change

△: Deterioration of film and lowering of hardness

×: Partly peeling between film and substrate

[RESULTS]

The results are shown in Table 1.

Table 1

| Fluorine-containing polymer | US6,790,587 | | Present invention | | Substrate |
|---------------------------------|-----------------------------|-----------------------------|-----------------------------|-------------------------|-----------|
| | EXPERIMENT 1 | EXPERIMENT 2 | EXPERIMENT 1 | EXPERIMENT 2 | |
| | Before UV irradiation | After UV irradiation | Before UV irradiation | After UV irradiation | |
| Reflectance of one side of film | - | 1.9 | - | 1.3 | 5.0 |
| Pencil hardness | 5B | 5B | 2B | HB | - |
| Solvent resistance | × (Completely dissolved) | × (Completely dissolved) | × (Completely dissolved) | △ (partly dissolved) | - |
| Alkali resistance | × (Completely dissolved) | × (Completely dissolved) | × (Completely dissolved) | ○ (No change) | - |

DISCUSSION

The experimental results shown in Table 1 prove the fact that the photoresist prepared from the resin composition according to the US'587 does not have sufficient physical properties such as strength, surface hardness, and solvent resistance, which are required for the optical materials such as anti-reflection coating films and optical waveguides and are the problems to be solved by the present invention. On the other hand, the photo-curable resin composition of the present invention does not attain the sufficient properties before UV irradiation, but, after UV irradiation, apparently those properties are considerably improved.

Though the photoresist of US'587 is similar to the photo-curable resin composition of the present invention in the point that both compositions comprise a fluorine-containing polymer and a photoacid generator, the photo-curable resin composition of the present invention has remarkable and unexpected difference from the viewpoint that the physical properties of the photo-curable resin composition of the present invention are drastically changed before and after UV irradiation, while the photoresist of US'587 does not show such changes in physical behavior.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This day of *March 24, 2008*

by *Takayuki Araki*
Takayuki ARAKI

We, the undersigned witnesses, hereby acknowledge that Takayuki ARAKI is personally known to us and did execute the foregoing Declaration in our presence on:

Date: *March 25, 2008* Witness *Mihoko Ohashi*

Date: *March 25, 2008* Witness *Takuji Ishikawa*